Chemical Geology xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

Relationship between river water chemistry and shell chemistry of two tropical African freshwater bivalve species

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ARTICLE INFO

Keywords:
Freshwater bivalve
Sclerochemistry
Shell geochemistry
Sr/Ca
Mg/Ca
Ba/Ca
Mn/Ca

ABSTRACT

Both climate change and land-use changes represent serious environmental issues throughout Africa, and are expected to lead to significant changes in river hydrology and geochemistry. Freshwater bivalve shell geochemistry may provide useful information about past river characteristics (discharge, geochemistry) providing a baseline to help understand modern environmental changes. Shells of two species of freshwater mussels (*Chambardia wissmanni* and *Aspatharia dahomeyensis*) were collected from two large African rivers (Oubangui and Niger Rivers) and were analyzed for Sr/Ca, Ba/Ca, Mg/Ca and Mn/Ca ratios along their maximal growth axis. Shell data were compared with geochemical data collected in these rivers every two weeks over a two-year period. To verify whether element ratios in shells were related to the host water, the elemental concentrations measured in the shells were set in a temporal context based on $\delta^{18}O_{shell}$ cycles. Shells from the Oubangui River to some extent recorded water element ratios, with variations in water Sr/Ca ratios being reflected in all three bivalve specimens analyzed, while only the youngest specimen exhibited complete coverage. The two older specimens recorded only segments of the water data, which suggests an influence of growth rate. This relationship was not observed in *A. dahomeyensis* shells from the Niger, suggesting a species-specific relationship between freshwater shells and water. The Ba/Ca and Mg/Ca record showed no similarity between the water elements and analyzed shells, but an ontogenetic decrease was observed in older specimens. Shell Mn/Ca ratios tracked pH in shells from the Oubangui, with a time-lag, which might be due to bivalves taking up the increased Mn via phytoplankton which are expected to show a similar time-lag. This relationship was not observed in shells from the Niger, where due to the high turbidity throughout the year we expect very low primary production rates. In conclusion, no consistent relationships between water chemistry and shell chemistry were observed. While Sr/Ca and Mn/Ca ratios in shells of *C. wissmanni* from the Oubangui were most promising as proxies of water chemistry, the utility of element ratios as tracers is compromised by species-specific effects or by site-specific phenomena.

1. Introduction

The African continent is highly vulnerable to the impacts of climate change, and the effects are broadly visible. In particular, the trends in annual-average near-surface temperatures over Africa for the past 50 years increased, especially over subtropical southern Africa, subtropical North Africa and parts of central tropical Africa (Engelbrecht et al., 2015). Increased temperatures affect the hydrological system and induce anomalies in rainfall, which in turn affect river discharge, the water source for much of Africa (De Wit and Stankiewicz, 2006). Africa's vulnerability to increase in droughts under climate change is expressed by recent severe droughts in the Sahel and in the Horn of Africa (Lyon and Dewitt, 2012) when the rainfall regime decreased (Lebel and Ali, 2009; Nicholson, 2013), resulting in both water scarcity and increased flooding in the Middle Niger River area due to soil crusting and decreased infiltration (Descroix et al., 2012a, 2012b). Tropical African rainforests also face consequences of drought, discontinuities in regional rainfall are more emphasized since the late 60s (Mahé and L'hote, 2001). As a result, severe decline in river discharge (Q) was observed in the past decades in the Oubangui River (Laraque et al., 2001; Orange et al., 1997; Runge and Nguimalet, 2005), and in the main stem of Congo River (Ladel et al., 2008; Laraque et al., 2001). To detect persisting trends in hydroclimate change, continuous measurements of the water geochemistry, hydrology, and material fluxes are very valuable. Unfortunately, these records are very scarce in Central Africa, long term discharge data exist only for few tropical

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https://doi.org/10.1016/j.chemgeo.2018.04.026
Received 14 September 2017; Received in revised form 5 March 2018; Accepted 20 April 2018
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rivers (Descroix et al., 2009; Laraque et al., 2001; Mahé et al., 2013), while measurements of other factors are even more scarce (Bouillon et al., 2012; Coynel et al., 2005; Seyler and Elbaz-Poulichet, 1995). Considering the lack of continuously measured data, robust proxies are needed to circumvent the missing environmental information necessary to understand the ongoing changes.

The wide availability of freshwater bivalves and their sequentially layered carbonate shell makes them a potential candidate for environmental proxies. The stable isotope composition of shell carbonate carries information about past water isotope variations since $\delta^{18}O_{shell}$ values are in isotopic equilibrium with water $\delta^{18}O$ values, which has been shown to be valid for marine (Epstein et al., 1953; Grossman and Ku, 1986; Chauvaud et al., 2005), and more recently freshwater specimens (Dettman et al., 1999; Kaandorp et al., 2003; Versteegh et al., 2010; Kelemen et al., 2017). Shell $\delta^{18}O$ values can be a good proxy for detecting hydroclimate changes by allowing the reconstruction of past water $\delta^{18}O$ values and/or recording discharge conditions during low (er) water levels (Kelemen et al., 2017; Versteegh et al., 2011). Riverine dissolved trace element concentrations also offer information about complex biogeochemistry of hydrological system, biological activity, residence time, water motion, weathering processes and pollution. In contrast to seawater, the elemental composition of freshwater is more complex and dynamic, and elements such as barium (Ba), strontium (Sr), manganese (Mn) and magnesium (Mg) play important roles in geochemical and biochemical processes (Négrel et al., 1993; Seyler and Elbaz-Poulichet, 1995; Elbaz-Poulichet et al., 1999). However, several authors have noted a relationship between elemental concentrations and river discharge: the concentration of cations (Ca^{2+}, Mg^{2+}) in the Oubangui River were found to follow the hydrological cycle (Probst et al., 1992) with minimum concentration during high discharge and maximum values reached during low flow. Similar observations were published for Sr and Ba as well (Seyler and Elbaz-Poulichet, 1995). In lack of continuous water measurements, bivalves has been recognized as extremely valuable archives from which environmental variability can be reconstructed. In several studies, trace element concentrations in freshwater shells were found to be proportional to the concentration measured in the waters in which the bivalve lived (Carroll and Romanek, 2008; Soldati et al., 2009; Zhao et al., 2015). Bulk analysis of *Margaritifera* shells revealed strong biochemical and geographical effects on the shell trace element composition and concentration, where the type and the trophic status of the river bear the strongest impact on trace element uptake (Bolotov et al., 2015). As bioaccumulators, bivalves directly take up elements from water, thus they can be a useful tool in determining metal concentration, but due to slower turnover, trace metals show different seasonal patterns in shells and in soft tissues (Ravera et al., 2007). There is also a difference in trace element composition between shell layers, Carroll and Romanek (2008) found that the elemental concentrations in the inner layer are higher than in the outer layer, although the feasible sampling resolution in the inner layer is much lower. Even if the main source of elements is the host water, biological controls can over-ride the environmental influences on trace element incorporation (Bailey and Lear, 2006; Izumida et al., 2011). Strontium has been proposed to serve as a proxy for past temperature if the Sr/Ca variability is small and known and if the age of the shell is taken into account (Izumida et al., 2011; Zhao et al., 2015). However, the relationship between strontium and temperature remains uncertain, some authors found it as positive (Izumida et al., 2011) while other studies reported a negative relationship (Zhao et al., 2015). Barium concentrations can indicate increased soil erosion, and since it usually varies in phase with Sr (Carroll and Romanek, 2008; Izumida et al., 2011; Risk et al., 2010; Soldati et al., 2009; Zhao et al., 2015), has been proposed to be an indicator for temperature changes. Despite the fact that both elements are liberated primarily by weathering, using Ba for paleotemperature reconstructions have been shown to be more complex, as food availability (Zhao et al., 2015) and growth rate (Izumida et al., 2011) may control the uptake. Manganese is suggested as a proxy for increased biological activity and indirectly for hydrological changes, as Mn peaks coincide with chlorophyll *a* increase in Lake Tanganyika during periodical upwelling (Langlet et al., 2007).

In this study, we examine the potential of *Chambardia wissmanni* and *Aspatharia dahomeyensis* shells as environmental archives by analyzing trace element composition deposited in carbonate shell layers. Bivalves collected in Bangui (Central African Republic, hereafter CAR) and Niamey (Niger) have been previously analyzed for stable isotopes (Kelemen et al., 2017), which allowed us to relate trace element patterns to time and thus to river conditions recorded every two weeks during the two years of monitoring. Our aims are to determine whether: (i) shell elemental ratios are synchronous between different individuals, and (ii) elemental ratios deposited in shell layers can be related to elemental ratios measured in the host water, and thus relate to discharge and/or water temperature in a predictable manner.

2. Materials and methods

2.1. Location and water sampling

The Oubangui River is the third largest tributary of the Congo River, originating from confluence of Uele and Mbomou Rivers. The Oubangui Basin is characterized with one dry and one wet season, the annual rainfall is 1400–1800 mm yr^{-1} resulting in single peak discharge. The basin's geological structure is mainly a vast peneplantion surface, represented with two major geological units: a basal complex (granite-gneiss, schist) and a sedimentary cover (sandstone, limestone), as well as well-developed ferralitic and ferruginous soils in the area (Négrel and Dupré, 1993).

The Niger River is the third longest African river with a length of 4700 km, crossing over five countries and ecologically divided into four hydrological subcatchment areas. Our study area is located in the Sahel (Middle Niger), where the annual rainfall is much lower than in the Oubangui catchment, ranging between 200 and 700 mm yr^{-1}. River water recharge is mainly rain-fed, thus the area is very sensitive to change. Long term droughts in the Sahelian area together with the land use changes caused the change of the hydrograph in the Niamey area, the one peak discharge regime became bi-modal (Descroix et al., 2012a, 2012b). The Middle Niger represents a boundary between two geological structures, the left bank is dominated by sedimentary terrigenous deposits, while the right bank lies in a granitic basement of the Liptako Gourma (Cappelaere et al., 2009). However, both areas are characterized with high sand and low silt and clay amount (Descroix et al., 2012). Soils are mainly of tropical ferralitic type, rich in sesquioxides (Al_2O_3 and Fe_2O_3), poor in organic matter (from 0.5% to 3%), and very prone to crusting (Descroix et al., 2012a).

From an economical and ecological perspective both rivers are equally important. Discharge records from the Oubangui and Niger River are available for several decades: continuous data recording started in 1929 and 1935 at Niamey and Bangui, respectively. Long term records revealed, that even though the two river basins are located in different ecoregions, with distinct watershed geology, the ongoing drought is perceptible in both ecosystems, at Bangui the discharge has significantly reduced in the past few decades (Nguimalet and Orange, 2013) while at Niamey the local flooding is more accentuated (Descroix et al., 2012a) despite the rainfall deficit of about 30% relative to the 1950–1969 period (Lebel and Ali, 2009).

Sampling sites for both rivers were selected due to the availability of long-term discharge measurements, thus for Oubangui River biweekly sampling was held at Bangui (Central African Republic) and the Niger River was sampled at Niamey (Niger). At both sites a two-year monitoring was conducted, at fortnightly intervals, at Bangui between March 2010 and November 2012, at Niamey between April 2011 and March 2013 (more details can be found in Kelemen et al., 2017). Water samples for element concentrations were taken further from the river shore with a polypropylene sampling bottle submerged 0.5 m below the

water surface. Samples were filtered on a 0.2 µm Sartorius Minisart polyethersulfone (PES) syringe filter, and stored without further preservation.

2.2. Water analysis

Water temperature and pH were measured in situ with a YSI ProPlus multimeter, whereby the pH probe was calibrated on each day using buffer solutions 4 and 7 (United States National Bureau of Standards). Total suspended matter (TSM) was monitored onsite during biweekly sampling and calculated by weighing precombusted 47 mm Whatman GFF before and after filtration. $\delta^{18}O_w$ and temperature data were presented previously in Kelemen et al. (2017), and physico-chemical and TSM data (along with other relevant data, e. g. alkalinity, pCO2) for the Oubangui were previously presented in Bouillon et al. (2014). pH data for the Niger River were provided by the SEEN (Société d'Exploitation des eaux du Niger). Trace element concentrations were measured by ICP-AES (Iris Advantage, Thermo) or ICP-MS (Agilent 7700×). For quality assurance, reference standard solutions with certified concentrations were analyzed: SRM1643e (NIST) and SPS-SW2 (Spectrapure). As an internal standard Au and Y were used for measurement with ICP-AES, while Ge was used as an internal standard on the ICP-MS. Measured data were always within 5.2% relative standard deviation for strontium and barium and 3.5% for calcium, magnesium and manganese of the average values of measured NIST standard, while for the Spectrapure standard, the values were better than 6.6% for Sr and Ba and 3.3% for Ca, Mg and Mn.

2.3. Shell analysis

A series of elements (Sr, Ba, Mn, Mg) and element-to-calcium ratios were examined at high resolution in unionid bivalve shells. Shells were collected during the years of water monitoring on several occasion from Oubangui and Niger River. Three *Chambardia wissmanni* shells from the Oubangui River were analyzed (one shell collected in 2012, two in 2013), and two *Aspatharia dahomeyensis* collected in the Niger in 2013 were analyzed.

One valve of each shell was cut along the maximum growth axis to achieve the highest possible sampling resolution. Thick sections were mounted on glass slides with two phase epoxy, fine polished and the outer prismatic layer was spot – drilled using New Wave Micromill for stable isotope measurements. The detailed sampling and analyzing procedure for stable isotope measurements ($\delta^{18}O$ and $\delta^{13}C$) along with the results are described in Kelemen et al. (2017).

For elemental analyses, the same sections sampled for isotopes were used. High-resolution trace element analysis of all thick shell sections was carried out at Union College (Schenectady, NY, US) on a LA-ICP-MS (Laser Ablation Inductively Coupled Mass Spectrometer) using a Perkin Elmer Elan 6100 DRC Inductively Coupled Plasma Mass Spectrometer coupled to a on a CETAC LSX-213 frequency quintupled Nd:YAG laser (λ = 213 nm) following Gillikin and Dehairs (2013). Trace elements were analyzed in the spots from the isotope sampling, the laser was shot directly in holes created by drilling for isotope analysis, hence all isotope and trace element profiles are completely aligned. Helium was used as the carrier gas (600 mL/min), which was mixed with argon after the ablation cell (840 mL/min). A spot size of 50 µm was used with the laser set at 10 Hz and 600 burst counts. The analysis time was 120 s, including 15 s pre-ablation for gas blank correction, when the shutter was closed and only the gas was measured. ThO/Th ratios were monitored daily, using the NIST 612 glass standard and were < 0.6%. For calibration the NIST 612 glass standard reference material was analyzed, while the USGS standard MACS-3 was used to check the calibration, at the start of the analysis and after approximately every 50 analyses. The reproducibility of the USGS MACS-3 carbonate standard (n = 8–24 per day) was better than 5% (percent relative standard deviation; % RSD) for Sr, Mn, Ba and Mg. At the start and end of each measurement day an additional carbonate standard, USGS MACS-1 was analyzed as an extra calibration control. The reproducibility was better than 5% over the day for Sr, Mn, and Ba.

The software package Iolite (iolite-software.com) was used for the reduction of data obtained by LA-ICP-MS. Iolite is implemented as a package for Igor Pro (data analysis program developed by WaveMetrics). Trace element analysis in Iolite is based on internal standard normalization and as an internal standard Ca was used (with a content of 40.04% for carbonates).

Measured water $\delta^{18}O$ values in combination with temperature can be used to calculate expected shell $\delta^{18}O$ (model shell) values, following the equation calculated by Dettman et al. (1999). Shells were always drilled starting from the ventral tip (most recently deposited carbonate) towards the umbo, and knowing the date of mussel's death allowed aligning the shell record with the water (see Kelemen et al., 2017 for full details). Calculated model shell was used to tune shell $\delta^{18}O$ values with the water $\delta^{18}O$ record. For the easier alignment, Julian days were used as a unit (t = 0 was 01.01.2010).

3. Results

3.1. Water

Water stable isotope values, water temperature, and discharge in both rivers were presented in Kelemen et al. (2017) and pH and TSM for the Oubangui River are discussed in Bouillon et al. (2012, 2014). The aqueous concentrations of Ca, Mg, Ba and Sr showed a clear difference in range and seasonality between the two rivers. Mn concentrations in Oubangui River were below quantification limit, thus those results will not be used for further discussion. Mn concentration in the Niger was measured only for the part of the samples collected during the monitoring time. Average concentrations with minima and maxima are displayed in Table 1 for the monitoring period, together with the measured pH and total suspended matter (TSM) concentrations. The concentration of elements in Oubangui River followed the cyclicity of $\delta^{18}O_w$ and pH, while they were inverse to the discharge trend and TSM cycles (Fig. 1). Elements were in phase with one another, although the range of Ba concentration was less pronounced in comparison with the other elements. In the Niger River, all elements were present in higher concentrations, but only Ca and Mg showed some cyclicity (Fig. 2). Elemental concentrations were still at maximum during low flow, but several high values were measured during the first discharge peak, which was not the case in the Oubangui River. In contrast to the Oubangui River, Sr and Ba in the Niger were not in phase.

3.2. Shells

Shells from the two sites exhibited different concentration ranges. In the shells from Niger River the range was nearly half of those from the Oubangui River, without evident cycles, or visible co-variation between

Table 1
Average element and total suspended matter concentrations and pH in both rivers (numbers in parentheses represent ranges, BDL = below detection limit).

River	Mg (mg/L)	Ca (mg/L)	Sr (mg/L)	Ba (mg/L)	Mn (µg/L)	TSM (mg/L)	pH
Oubangui (Bangui)	1.68 (0.99–3.02)	3.88 (2.38–7.24)	0.02 (0.01–0.03)	0.02 (0.02–0.03)	BDL	14.6 (2.0–33.2)	7.32 (6.45–8.24)
Niger (Niamey)	1.87 (1.29–3.00)	3.89 (2.78–5.98)	0.06 (0.03–0.19)	0.08 (0.01–0.2)	1.78 (0.30–5.29)	223.8 (18.2–1578)	7.49 (7.05–8.01)

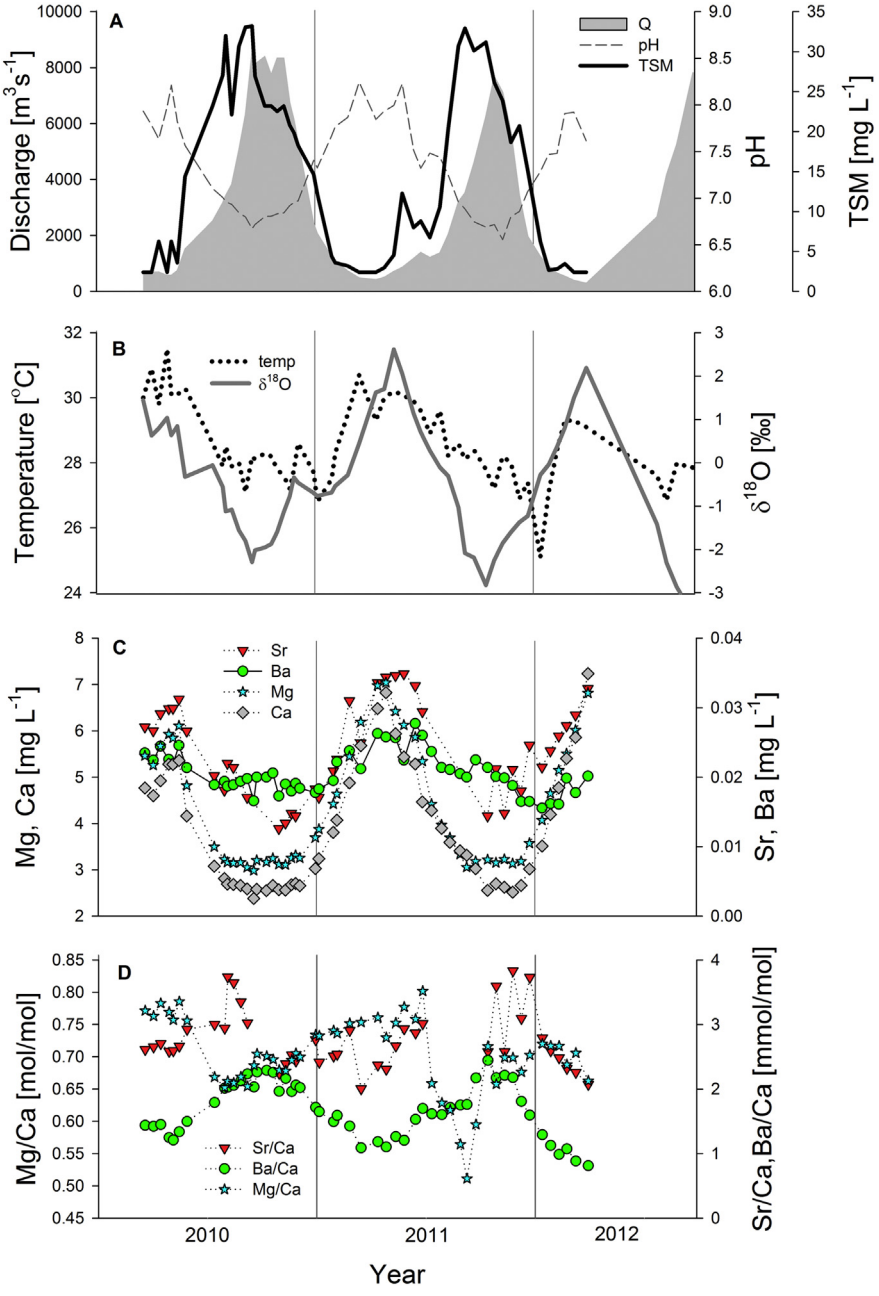

Fig. 1. Water chemistry in the Oubangui River. Data from two years of monitoring between April 2011 and March 2013. A-daily discharge (grey-shaded area) plotted with pH (grey dashed line) and TSM (black solid line); B- $\delta^{18}O_w$ (grey solid line) plotted with temperature (black dotted line); C-dissolved element concentrations; D-element-to-calcium ratios.

the shells (Table 2). Time resolution in the shell data was determined from the $\delta^{18}O_{shell}$ record (see Kelemen et al., 2017), thus element profiles could be compared between shells and environmental parameters. Unlike $\delta^{18}O_{shell}$ values with distinct seasonality, element profiles in these bivalves showed no particular cycles (Fig. 3). Only Mn/Ca profiles from the Oubangui shells could be related to $\delta^{18}O_{shell}$ seasonality, thus Mn/Ca ratios were in phase for the three analyzed shells from Oubangui (Figs. 1, 5). The highest similarity was found in the BB6 shell where the Mn profile clearly followed the cyclicity of the water $\delta^{18}O$ values. The other two shells had more scattered data, but still recognizable correlation. For the Niger River shells, the relationship between Mn/Ca ratio and $\delta^{18}O$ seasonality is less clear than in the shells from Oubangui River, although the Mn/Ca pattern of shell N37 was matching with the water pH (Figs. 2, 6). Other element-to-calcium ratios measured in the shells were not clearly in phase with the water elements nor with measured pH or TSM concentrations, except the three shells from the Oubangui River, which showed some similarities in Sr/Ca ratios, but were not in obvious phase with each other (Fig. 3). Only part of the record in shells were in phase with the water Sr/Ca data, water Sr/Ca peak values were recorded by shells, although only one by each shell. While the juvenile shell BB6 had the best correlation almost over the entire record. None of the other elemental ratios were comparable with the other shells, but within shell Sr/Ca and Ba/Ca ratios were mainly in phase. Oubangui shells showed stronger visual parallel but weaker statistical correlation, the strongest correlation within Oubangui samples was in 2B shell ($R^2 = 0.29$, $p < 0.0001$), for the rest there were only very weak correlations ($R^2 < 0.07$, $p < 0.0001$). Sr/Ca and Ba/Ca ratio were in phase in the two bivalves from the Niger River (Fig. 4), with a strong correlation for N50A ($R^2 = 0.71$, $p < 0.0001$) and a bit less strong correlation in N37

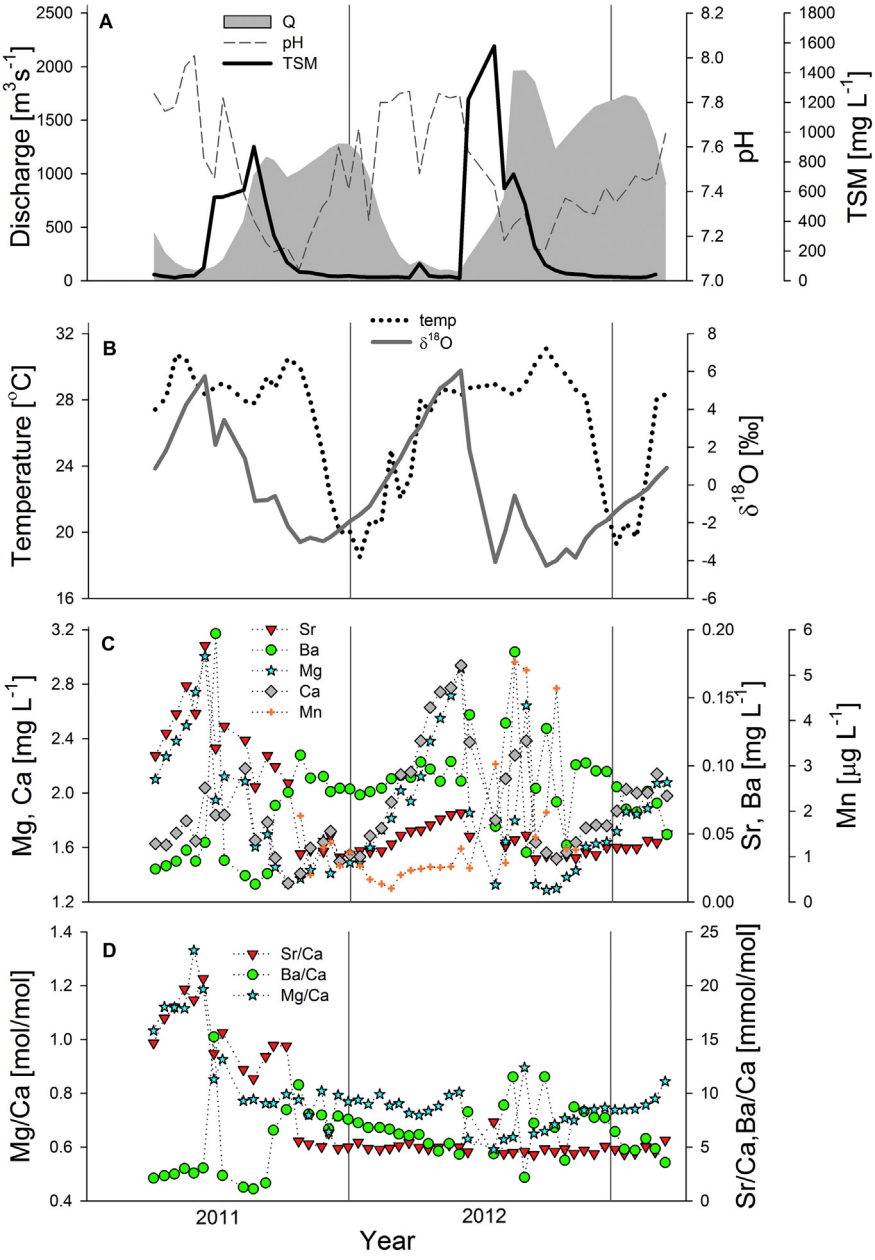

Fig. 2. Water chemistry in the Niger River. Data from two years of monitoring between April 2011 and March 2013. A-daily discharge (grey-shaded area) plotted with pH (grey dashed line) and TSM (black solid line); B-$\delta^{18}O_w$ (grey solid line) plotted with temperature (black dotted line); C-dissolved element concentrations; D-element-to-calcium ratios.

Table 2
Shell element ratios from both rivers. Ranges are representing the data from the three analyzed shells from the Oubangui River and the two shells from Niger River.

River	Mg/Ca (mmol/mol)	Mn/Ca (mmol/mol)	Sr/Ca (mmol/mol)	Ba/Ca (µmol/mol)
Oubangui (Bangui)	0.06–0.79	0.29–5.01	0.5–1.21	52.1–139.9
Niger (Niamey)	0.04–0.37	0.07–1.98	0.65–1.34	59.9–168.8

($R^2 = 0.59$, $p < 0.0001$).

4. Discussion

4.1. River elemental profiles

The Oubangui River is characterized by a one peak discharge regime, with highest discharge during the rainy season from September to November and with lowest values between March and April (Fig. 1). $\delta^{18}O_w$ values mirror the discharge seasonality, forming a distinct sinusoidal curve (values ranged between −3.7‰ and +2.6‰), with the most positive values during the dry season and negative peaks during the wet period (Kelemen et al., 2017). Profiles for all dissolved elements were synchronized with the $\delta^{18}O_w$ record and vary inversely with discharge, exhibiting a nearly perfect sinusoidal curve (Fig. 1C). Dissolved element concentrations were lowest at high water discharge, increased

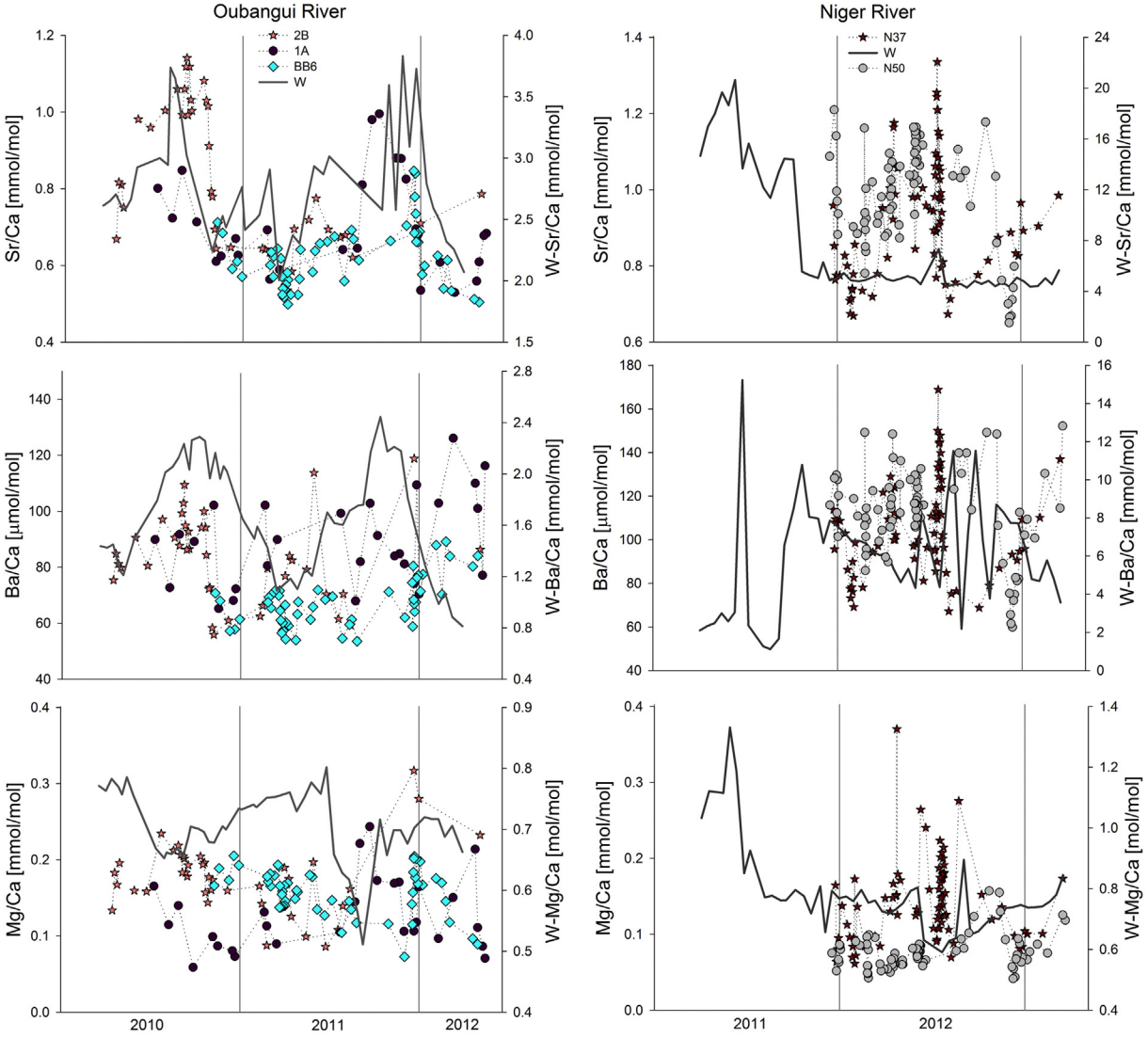

Fig. 3. Shell and water element/Ca ratios from Oubangui (left) and Niger (right) Rivers. The various symbols representing different specimens, but each symbol belongs to one specimen in all three graphs. The solid grey line represents the water element-to-calcium ratio.

during falling river stage and reached the highest concentrations at low discharge. This pattern is likely a result of dilution of the river water by rain and surface waters (Probst et al., 1992). However, a study using strontium isotope ratios of dissolved and suspended loads revealed that the decrease of major and trace element concentrations during increasing discharge in the Oubangui River cannot be explained simply by dilution of the base flow by an input of rain water, because even if the element concentrations decrease, chemical weathering increases (Négrel and Dupré, 1993). Seyler and Elbaz-Poulichet (1995) suggested that in the Oubangui River two weathering end members exist: silicate weathering dictates the element load during high discharge, while during low flow, carbonate weathering dominates the element load. Négrel et al. (1993) suggest that the pattern in the Oubangui is driven by different water sources during wet and dry seasons. The Uele river is the principal tributary of the Oubangui river at the time of low water period (Négrel and Dupré, 1993), while during the wet season the tributaries from the North provide the majority of the discharge, which are mainly surface runoff and provide a significant supply of elements (Probst et al., 1992). Dissolved element concentrations exhibited seasonal cycles, inverse to discharge seasonality, the relationship best fit a logarithmic regression: $R^2 = 0.87$ for Ca, $R^2 = 0.85$ for Mg, $R^2 = 0.73$ for Sr (for all three: $p < 0.0001$) and the lowest correlation of $R^2 = 0.19$ was for Ba ($p < 0.002$).

Dissolved element-to-calcium ratios in the Oubangui River show a less clear relationship with discharge (Fig. 1). This is clearly due to the close synchronization between Ca and the other elements. Ba/Ca ratios in the Oubangui River show the clearest seasonal variation, with peaks during high discharge (the inverse of Ba concentrations). Thus, Ba/Ca ratios follow the seasonality of Q while Ba is in phase with $\delta^{18}O_w$ cycles. This exceptional behavior of Ba concentration suggests that perhaps an additional source of Ba exists in the Oubangui River in addition to weathering. Sr/Ca ratios exhibited much more scatter with a much less clear seasonality. However, like Ba/Ca ratios, the highest Sr/Ca ratios occurred during high discharge and varied by nearly 2 mmol/mol. Similarly, Mg/Ca ratios also showed a seasonal cycle, but were inverse to both Ba/Ca and Sr/Ca ratios. Mg/Ca ratios slowly increased during the sampling period except approximately 2 months before the peak discharge, when the ratio dropped to its minimum value. Mg/Ca ratios varied by nearly 300 mmol/mol over the sampling period. While element-to-calcium ratios in the Oubangui River were less sinusoidal than dissolved element concentrations, they all exhibited somewhat of a seasonal cycle and all significantly varied.

Niger River dissolved elements differ in many aspects from the Oubangui River, which can be related to the different hydroclimate of this region. Since the beginning of the drought in 1970's in Africa, the single peak hydrograph divided into two. The first discharge peak

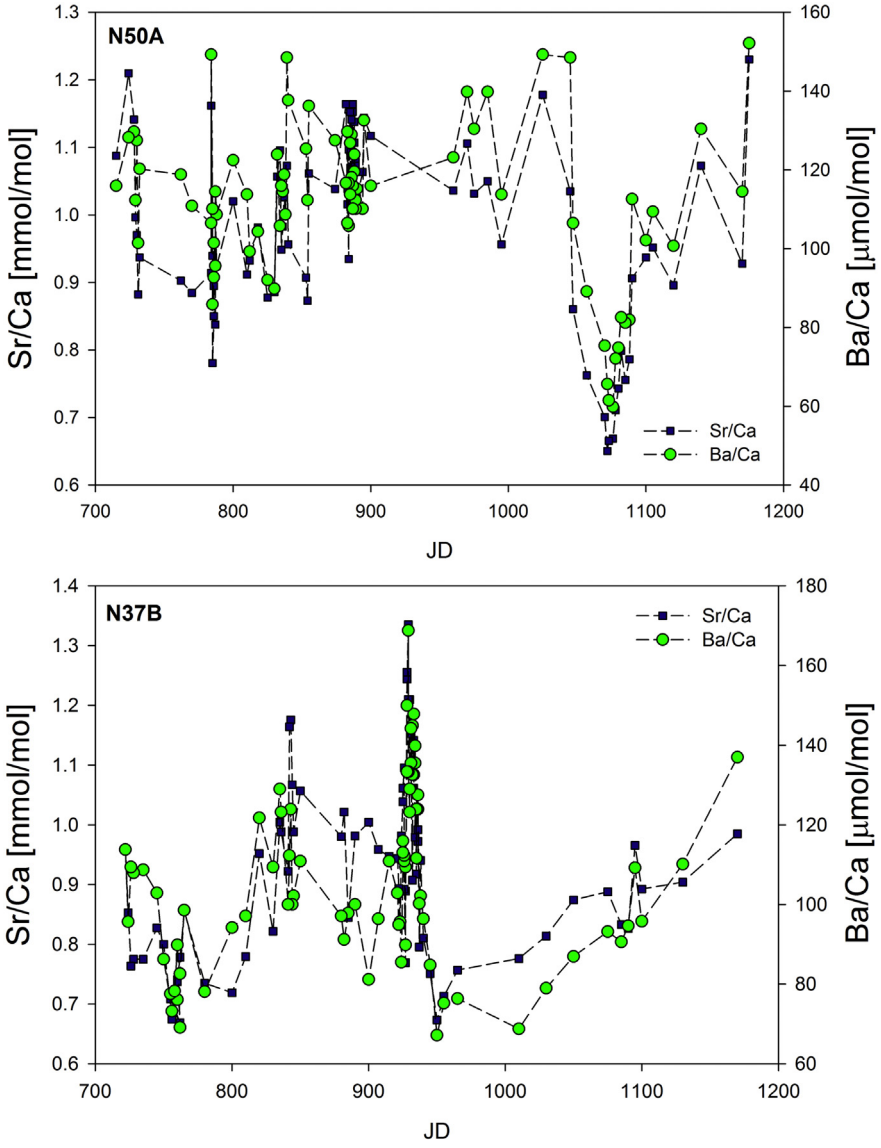

Fig. 4. Sr/Ca (green circles) plotted with Ba/Ca (blue squares) ratios in the two shells from the Niger River. In both specimens the relationship was linear, with a strong correlation: $r^2 = 0.71$ in N50 and $r^2 = 0.59$ in N37. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

arrives with the heaviest monsoon rainfall in August, being mostly transported by three local Sahelian tributaries (Gorouol, Dargol and Sirba Rivers), and is known as the "red flood" because of its sedimentary load arising from the erosion of local iron oxide rich soils. The second (main) flood starts in November, having a low sediment load and originating from the upstream part of the Niger River (Descroix et al., 2012a). As can be seen on Fig. 2A, the highest concentration of TSM is measured just before the arrival of the first peak discharge, while the second peak causes almost no change in suspended matter concentration. The spike in the suspended load generally coincides with a decrease in dissolved Sr, Mg, and Ca and an increase in Ba, although this pattern varies somewhat between the two years (Fig. 2). Moreover, Sr and Ba in the Niger vary considerably more than in the Oubangui (between 0.05 and 0.2 mg/L vs. 0.01 to 0.03 mg/L), whereas Ca and Mg show a larger range in the Oubangui (between 1 and 3 mg/L vs. 2 to 7 mg/L). Although variations in the dissolved element load of the Niger vary in a complex manner, element concentrations were the highest during low water conditions similar to elements in the Oubangui River (Fig. 2). Dissolved element-to-calcium ratios in the Niger show no clear seasonality. For example, Sr/Ca ratios are nearly constant for the last 1.5 years of sampling. The discharge in the Niger River is supplied by different water sources, carrying a complex seasonality of dissolved elements, although highest concentrations in both years were coinciding with the lowest discharge period.

4.2. Shell elemental profiles

Depending on the habitat (marine or freshwater), bivalves precipitate their carbonate shell from water with different element concentrations and in the form of two major polymorphs: aragonite and calcite (e.g., Lorens and Bender, 1980). The polymorphs are differing in their organization and orientation of carbonate molecules and incorporation mechanisms, likewise in affinity towards different size of cations – aragonite is prone to incorporate larger molecules than calcite (Morse and Bender, 1990; Falini et al., 1996). Minor element incorporation into abiotic calcium carbonates is mainly in control of lattice structures, which can occur through a simple ion substitution for Ca or through co-precipitation of another carbonate (e.g. $MgCO_3$, $SrCO_3$), as their ionic radius is similar to that of Ca (Morse and Bender, 1990). High correlations (positive or negative) among elements such as

Sr, Mg and Ba suggest a common mode of incorporation, while uncorrelated elements such as Mn probably differ in their inclusion site (Campana, 1999). As the trace elements are being incorporated along with Ca to build the CaCO3 structure, they are usually incorporated in proportion to the element to Ca ratio in the calcifying fluid with a thermodynamic partition coefficient (e.g., Gaetani and Cohen, 2006). Thus we focus our discussion on the relationship between element to Ca ratios in the water to those in the shell. If shell elemental ratios were dependent on elemental concentrations in the water, we would expect a close correlation between shell elemental ratios and $\delta^{18}O$ values because the shell $\delta^{18}O$ values track water $\delta^{18}O$ values, which correlate with elemental concentrations. We did not observe any correlations between shell elemental ratios and $\delta^{18}O$ values, thus it is unlikely elemental concentrations on their own impact shell chemistry.

4.2.1. Strontium

Controls on strontium incorporation into the calcareous skeleton of bivalve shells has long been a focal point for many studies, but results remain contradictory. In addition to the available Sr in the water, the organization and orientation of the carbonate molecules also impacts the amount of elements that will be incorporated in the $CaCO_3$ structure. Studies show that the incorporation of Sr^{2+} into abiotic aragonite is about two orders of magnitude higher than into abiotic calcite (Lorens, 1981; Tesoriero and Pankow, 1996), possibly because aragonite incorporates larger cations than calcite (Falini et al., 1996). Strontium carbonate is virtually isostructural with aragonite, thus substitution of Sr for Ca is the most likely pathway of Sr incorporation (Greegor et al., 1997). While marine environments have a more stable Sr^{2+} concentration, river water chemistry is directly influenced by the bedrock geology through weathering. Early studies on marine bivalves reported temperature dependence on Sr/Ca incorporation but the relationships varied widely (Gillikin et al., 2005; Surge and Walker, 2006; Wanamaker et al., 2008). Others suggested strong biological and kinetic effects as the main control for Sr/Ca ratios (Gillikin et al., 2005; Lorrain et al., 2005). In tropical freshwater systems with small changes in water temperature and large variations in dissolved element load, shells ideally should track water chemistry. Indeed, Zhao et al. (2015) show that Sr/Ca ratios in freshwater *Corbicula* shells increase in a linear fashion over a ~10 mmol/mol range ($R^2 = 0.922$). Shells from our study showed no temperature dependence on Sr incorporation. Specimens from the Oubangui exhibited some correlation with water Sr/Ca ratios (Fig. 3). Shell Sr/Ca ratios track water ratios in shell BB6 from the Oubangui, whereas shell 2B only captured the peak in 2010, while shell 1A the peak in 2011/2012 (Fig. 3, Fig. S1-supplementary material). However, this may be due to sampling resolution. Shells 2B and 1A were collected in 2013 and were estimated to be 6 and 5 years of age (based on $\delta^{18}O_{shell}$ cycles; Kelemen et al., 2017), which will have lower growth rates than younger specimens (such as shell BB6). Lower growth rates result in more time averaging (each analytical data point represents more time) and drive the environmental signal recorded in the shell towards mean values. Füllenbach et al. (2017) reported the importance of high resolution measurements, as layers with different strontium content changing approximately every 1–5 µm, thus with the usual 50 µm laser spot diameter strongly elevated or reduced Sr concentrations might remain undetected. Moreover, the water monitoring period covered only the last 2 years of shell growth, which might explain the co-variation with only one peak value of water Sr/Ca ratio in these two shells (Fig. S1-supplementary material); shell growth in the last year of life for shell 2B was slower than in shell 1B. In contrast to the older specimens from the Oubangui River, the Sr/Ca ratio of juvenile shell BB6 showed an exceptional co-variation with water Sr/Ca ratios, which was in phase for the entire record, but due to short lifetime of this bivalve only one of the peak and approximately 2/3 of the water Sr record was detected (Fig. S1-supplementary material). This is in agreement with findings of other studies on concentration dependence of Sr incorporation, where shell Sr/Ca ratios increased linearly proportional to Sr/Ca ratio of the water in specimens grown under controlled laboratory conditions (Lorens and Bender, 1980; Zhao et al., 2015) but also in freshwater mussels captured from natural habitats (Carroll and Romanek, 2008).

In contrast, the shells from the Niger river do not show a clear relationship between strontium in shells and water (Fig. 3). In additon, shell Sr/Ca ratios show considerable variation during the last 1.5 years of the monitoring period while the water Sr/Ca ratios were essentially constant. This would suggest that water Sr/Ca ratios are not the dominant control on shell Sr/Ca ratios in *A. dahomeyensis* shells from the Niger River and that there are likely strong species-specific effects on freshwater mussel shell Sr/Ca ratios.

Several authors have suggested that shell growth rate plays a major role in Sr incorporation (e.g., Gillikin et al., 2005; Lorrain et al., 2005). Gaetani and Cohen (2006) achieved similar results precipitating synthetic aragonite, where during the fast growing phase higher amount of Sr were incorporated than during slow growth. In addition, Izumida et al. (2011) concluded that growth rate affects Sr/Ca ratios in *Hyriopsis* freshwater bivalves. This would suggest that Sr incorporation in shells is kinetically controlled. Indeed, the two older shells from the Oubangui River (2B, 1A) show a decrease in Sr/Ca over their lifetime (Fig. S2-supplementary material). However, other experimental studies observed an increase in Sr/Ca ratio with precipitation rate (Lorens, 1981; Mucci and Morse, 1983; Tesoriero and Pankow, 1996), and others suggested that kinetic control does not affect Sr/Ca ratios in synthetic aragonite (Mucci et al., 1989; Zhong and Mucci, 1989). Gillikin et al. (2005) found a significant correlation between the growth rate and Sr/Ca ratio in *Saxidomus giganteus* shells, while in the same study *Mercenaria mercenaria* did not show the same consistency, thus the authors suggested that Sr/Ca ratios in shells are not under direct control of growth rate. If Sr incorporation would be under kinetic/growth control, it would be expected that the highest strontium concentrations occur during the fast growth period (in juvenile shells), but in our study, daily growth rate showed no correlation with Sr/Ca ratio, which is in agreement with the findings of Füllenbach et al. (2017) in *Cerastoderma edule* shells and Zhao et al. (2015) in *Corbicula fluminea* shells. Although older specimens showed some level of ontogenetic decrease, the younger faster growing BB6 shell did not exhibit higher Sr/Ca ratios, thereby suggesting growth rate is not the dominant control in these shells. While we cannot present a clear driver of Sr/Ca ratios in these African freshwater shells, it is clear they are not all robust recorders of Sr/Ca ratios in the river water and that each species should be evaluated independently.

4.2.2. Barium

The Ba concentration profile of aragonite shells has been proposed as a useful proxy for aquatic primary productivity, since Ba concentrations of shell aragonite may reflect the ingested Ba-rich phytoplankton (Stecher et al., 1996). Many authors indicated that shell Ba/Ca peaks are formed shortly after phytoplankton blooms, thus they can indicate primary production peaks, and can be used to provide a time axis for geochemical data in shells (Gillikin et al., 2006, 2008; Goodwin et al., 2013; Vihtakari et al., 2017). In this study, shell Ba concentrations could not be directly linked to primary production due to lack of chlorophyll *a* measurements. However, Bouillon et al. (2012) suggested higher phytoplankton abundance during low flow conditions in the Oubangui, which may explain part of the observed dissolved Ba cycle. Although all shell Ba/Ca record showed clearly distinguishable peaks, peak values could not be related to the water Ba/Ca record (Fig. 3, Fig. S3-supplementary material). Moreover, large interspecimen variations were observed in the Ba/Ca ratios, suggesting they are not recording an environmental signal as also suggested by Goodwin et al. (2013).

In marine shells of *Mytilus edulis*, large Ba/Ca peaks appeared in early life stage of the bivalves, while in older shells Ba/Ca ratios generally lacked large Ba/Ca peaks, which was interpreted as physiological effect of ageing (Vander Putten et al., 2000; Gillikin et al., 2006).

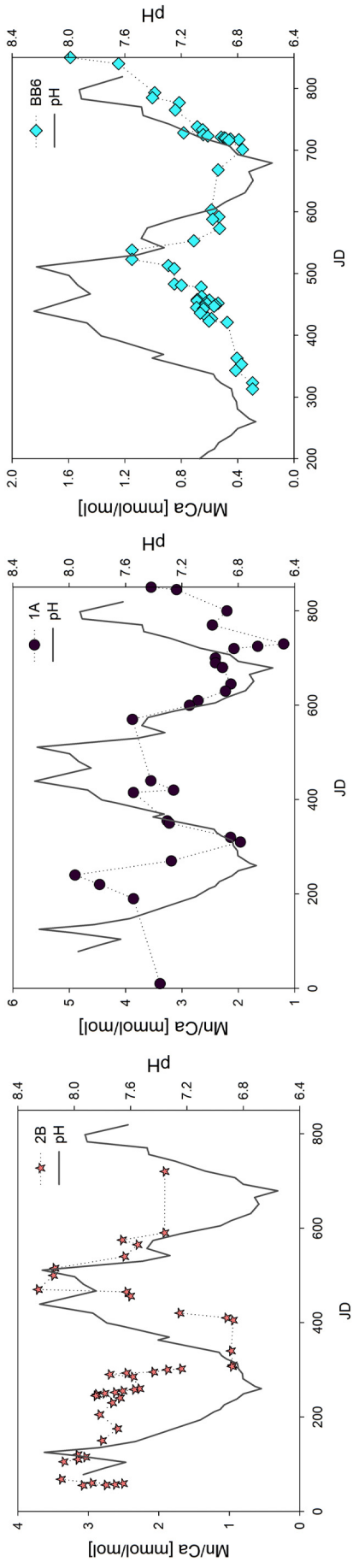

Fig. 5. Mn/Ca ratios of the three *C. wissmanni* shells (various symbols) from the Oubangui River plotted with water pH (solid line). The x-axis represents Julian date (JD), calendar days, starting from Jan 01, 2010,derived from the $\delta^{18}O$-based age models.

Izumida et al. (2011) also suggested Ba/Ca was under physiological control in the freshwater species *Hyriopsis*, where the shell Ba/Ca ratio was positively correlated with temperature, which is contradictory with expectations for thermodynamic partitioning (Gaetani and Cohen, 2006), thus Ba incorporation is possibly under control of growth rate. The two old(er) shells from Oubangui River (2B, 1A) showed an ontogenetic decrease in the amplitude of Ba/Ca peaks over the years, similar to the Sr/Ca and $\delta^{13}C$ record. This could be explained by different life stage in which the selected bivalves were, with the young specimens incorporating more of the available Ba.

High intra shell similarity was observed between shell Sr/Ca and Ba/Ca records. Visually shells from both rivers showed high similarity, although the correlation in the shells from Oubangui River were rather poor: 2B ($r^2 = 0.29$; $n = 144$), 1A ($r^2 = 0.07$; $n = 102$) and BB6 ($r^2 = 0.07$; $n = 57$), shells from the Niger River showed an exceptional correlation: N50A ($r^2 = 0.71$; $n = 83$) and N37B ($r^2 = 0.59$; $n = 90$) (Fig. 4). Both specimens from the Niger River were in the early stage of life, which might suggest a growth rate/life stage dependence of incorporation of these elements. However, the young specimen from the Oubangui River showed no correlation, thus growth rate is most likely not the determining factor of coinciding Ba and Sr metabolism. However, both specimens from Niger River belong to *A. dahomeyensis*, which suggests that the Sr/Ca-Ba/Ca relationship is species-specific. Thus, further study of the physiology and calcification mechanism of *A. dahomeyensis* is paramount to understand the factors behind the simultaneous metabolism of these two elements.

4.2.3. Magnesium

Several authors have reported a strong correlation between sea surface temperature and Mg/Ca ratio (Freitas et al., 2005, 2012; Klein et al., 1996; Lazareth et al., 2003; Schöne et al., 2011), but while some found a positive Mg/Ca – temperature relationship (Vihtakari et al., 2017; Wanamaker et al., 2008;) others reported negative correlation (Schöne et al., 2011). Ontogeny has been also proposed as a controlling factor for Mg incorporation (Freitas et al., 2005). In the older specimens analyzed from Oubangui River (2B, 1A) a slight ontogenetic decrease has been observed. This is in agreement with the findings of Takesue and van Geen (2004) that slower growing and organic rich layers are more depleted in Mg. For the shells from the Niger River the same approach could not be applied, considering the short lifetime of the specimens (~2 years). None of the shells investigated in this study showed seasonal pattern in Mg/Ca ratios, nor do shell Mg/Ca variations reflect water Mg/Ca changes despite large changes in water chemistry. No temperature dependence of Mg incorporation has been found nor growth rate could be related to Mg/Ca. Temperature dependence of Mg incorporation has been so far reported only for marine specimens, with significant variation among different species. Thus, assessment of the physiology and the calcification mechanism of investigated specimens are needed to decipher the mechanisms responsible for Mg incorporation. Freitas et al. (2005) reported, that in *Pinna nobilis* shells the best fit between the temperature and shell Mg/Ca ratio is during the first 4–5 years of growth, after which ontogenetic effects decouple the relationship. Thus the fluctuations of Mg/Ca ratio observed in the analyzed shells might reflect physiological effects, metabolic control, or contamination with organic material during precipitation.

4.2.4. Manganese

Seasonal fluctuation of seawater Mn concentrations has been proposed to be the dominant control on shell Mn concentrations in marine shells (Barats et al., 2008; Freitas et al., 2006). Manganese is a trace element actively involved in redox processes and is the most soluble in its reduced Mn(II) form. Dissolved Mn is slowly removed from the water column by oxidation, sorption onto inorganic and organic particles, or bacteria and phytoplankton uptake (Klinkhammer and McManus, 2001). An increase of biological activity at the time of high availability of Mn in surface waters likely enhances the production of Mn-rich

particles, while certain algae types can efficiently accumulate Mn^{2+} intracellularly (Sunda and Huntsman, 1985). Phytoplankton blooms have been associated with an increase in suspended particulate Mn in seawater (Sunda and Huntsman, 1988) and with increase in pH, which enhances carbonate precipitation (Richardson et al., 1988). Seyler and Elbaz-Poulichet (1995) reported that in the Oubangui River, trace elements such as Mn show a maximum concentration during the decreasing stage two months after the peak discharge, and a Mn concentration increase had been accompanied by a decrease of pH and an increase in nutrients. Although we are not in possession of recent measurements of water Mn concentration to compare (measured concentrations were below the detection limit of our method), shell Mn/Ca records showed similar cycles as $\delta^{18}O_{shell}$ with being in a phase including a few weeks of delay (Fig. 5). The overall Mn/Ca patterns in all three specimens from the Oubangui River are similar, despite differences in the concentration levels and the ontogenetic trends (Fig. 5). Shell BB6 has the lowest concentration range, but the best correlation with $\delta^{18}O_{shell}$ data over the entire record. Manganese peak values are synchronized with $\delta^{18}O_{shell}$ with approximately 60 days of delay. Similarly, the other two shells (ontogenetically older than BB6) exhibited a good co-variance with $\delta^{18}O_{shell}$ record, although peak values were not always represented, and the delay between the two records was more variable (30–60 days). The differences in the concentration range of Mn/Ca between shells might be induced by different affinity towards Mn in different life stages, or young bivalves perhaps control their internal pH better than older specimens. Note that $\delta^{18}O_{shell}$ of every specimen analyzed has been tuned to $\delta^{18}O_w$, thus $\delta^{18}O_{shell}$ corresponds to $\delta^{18}O_w$ record, including the individual biological effects (growth rate, growth stops, age, etc.). In the Oubangui River records of $\delta^{18}O_w$ and pH are in phase (Fig. 1), thus the similarity between the $\delta^{18}O_w$/pH and shell Mn/Ca record suggest high pH sensitivity of Mn incorporation in these shells.

In the Oubangui River the highest pH was measured during low discharge when primary production expected to be at its maximum (Bouillon et al., 2012). If the manganese availability increases during the falling limb of the discharge peak (Seyler and Elbaz-Poulichet, 1995) and the phytoplankton colony requires some time to be formed and take up Mn, then the delayed Mn/Ca record in the shells may be associated with food supply and not necessarily with direct uptake of Mn from water. Thus, Mn in phytoplankton likely serves as a source for Mn incorporation in bivalve shells, which can serve as an explanation for the several weeks delay observed in these shells. Several studies on bivalves suggested phytoplankton blooms are a major source of Mn in shells (Vander Putten et al., 2000; Lazareth et al., 2003; Langlet et al., 2007). This hypothesis was consistent with the several weeks delay between the increased freshwater discharge rich in nutrients and Mn, and the higher Mn concentrations in *Isognomon ephippium* shells (Lazareth et al., 2003). Likewise, in Lake Tanganyika the highest Mn concentrations were measured in *Pleiodon spekii* shells during seasonal upwelling, when deep anoxic layers becoming available for biological assimilation by phytoplankton and filter-feeding bivalves (Langlet et al., 2007). Thus phytoplankton rich in Mn seem the most likely source of Mn in *C. wissmanni* shells from the Oubangui.

Shells from the Niger River did not exhibit synchronous Mn/Ca ratios and did not track water Mn/Ca ratios (Fig. 6). Instead, the shell Mn/Ca record appears to follow the opposite trend of the water Mn/Ca ratios, with the shells incorporating the least Mn during periods of high dissolved Mn. In the Niger River $\delta^{18}O_w$ and pH are roughly in phase, although in contrary to shells from Oubangui River, in these shells the Mn/Ca pattern was more consistent with pH than with $\delta^{18}O_{shell}/\delta^{18}O_w$ record. The Mn/Ca record of shell N37 was synchronized with water pH for its entire lifetime, while shell N50 (same species, same age) corresponded with pH over only part of the record and incorporated much lower amounts of Mn. A possible explanation for this is that the Niger River has high turbidity and high sediment rate, which is not preferred by phytoplankton. Imevbore (1970) noted that Niger River was especially poor in nutrients, essential for primary production. Since the phytoplankton production is not peak-like in the Niger River and pH fluctuations are of much smaller range, shells are probably incorporating Mn over the entire year, thus the missing manganese peak are likely a result of low primary productivity in this river. Fairly good correspondence of Mn/Ca ratio to pH suggesting that pH has a control on Mn incorporation in both species from these two rivers, which is consistent with the redox control on dissolved Mn, but due to high variation in shell Mn/Ca ratios, it cannot be used as a reliable proxy for pH reconstruction.

5. Conclusions

We present here the elemental data of five bivalve shells collected from two large African rivers alongside concomitant elemental and biogeochemical data from two years of water monitoring at both sites. Dissolved elements in the two river systems behaved differently, with elements in the Oubangui correlating to discharge, and a more complex pattern in the Niger. Nevertheless, elements and element ratios varied significantly in both rivers and thus should show responses in the shells. It is clear from this study that the two species differ significantly in element incorporation mechanisms: while in *C. wissmanni*, certain element-to-calcium ratios in shells showed a relationship with environmental factors, none of the elements measured in *A. dahomeyensis* specimens could be related to any measured parameter in the host water. Seasonal Sr/Ca variations of the Oubangui River were relatively well recorded by the shells from this river; the youngest specimen incorporated Sr tracking the entire water record, while older specimens recorded only segments, perhaps due to reduced growth and time averaging during sampling. Ba/Ca ratios were found to be insensitive to changes in environmental conditions, but older specimens exhibited an ontogenetic decrease, which suggest a metabolic control over this element. The two young specimens of *A. dahomeyensis* showed good intra shell correlation between Ba/Ca and Sr/Ca records, suggesting a species-specific incorporation of these two elements. Similarly, shell Mg/Ca ratios are found to vary between specimens and none of the measured water parameters could be related with the shell record. Shell Mn/Ca ratios have a potential as a proxy for water pH, highest Mn concentration in the Oubangui shells were measured 30 to 60 days after the peak pH values in water. This suggests that the primary Mn source is not the dissolved Mn^{2+} in the water, but possibly the ingestion of manganese rich phytoplankton. This is supported by shells from the Niger River, where the highest water concentrations of (dissolved) Mn were not recorded in the shells, instead, the Mn/Ca record was synchronized with water pH. Although there is an obvious effect of pH on the Mn concentration in shells, the lack of consistency in shell concentrations and the different correspondence to pH between the two rivers/two species (with and without time-lag) excludes Mn/Ca ratios as a reliable proxy for pH reconstructions.

Acknowledgements

Funding for this study was provided by the Research Foundation Flanders (FWO_Vlaanderen; research project G.0D87.14N, and travel grants) to S.B. and D.P.G., the European Research Council (ERC Starting Grant 240002, AFRIVAL) to S.B., a National Geographic Society Research and Exploration Grant (#8885_11) to D.P.G. and S.B., the KU Leuven Special Research Fund (DBOF/14/025, PhD scholarship to Z.K.), and a Research Corporation for Science Advancement Single Investigator Cottrell College Science Award (#20169) to D.P.G. We also thank the U.S. National Science Foundation for providing funding for Union College's Perkin Elmer ICP-MS (NSF-CCLI #9952410) and CETAC LSX-213 (NSF-MRI #1039832). We thank Dan Graf for the identification of bivalve specimens and Alhou Bassirou for providing the Niger pH data. Finally we thank Michael E. Böttcher (Editor-in-Chief), Fred Andrus (Guest Editor) and two anonymous reviewers

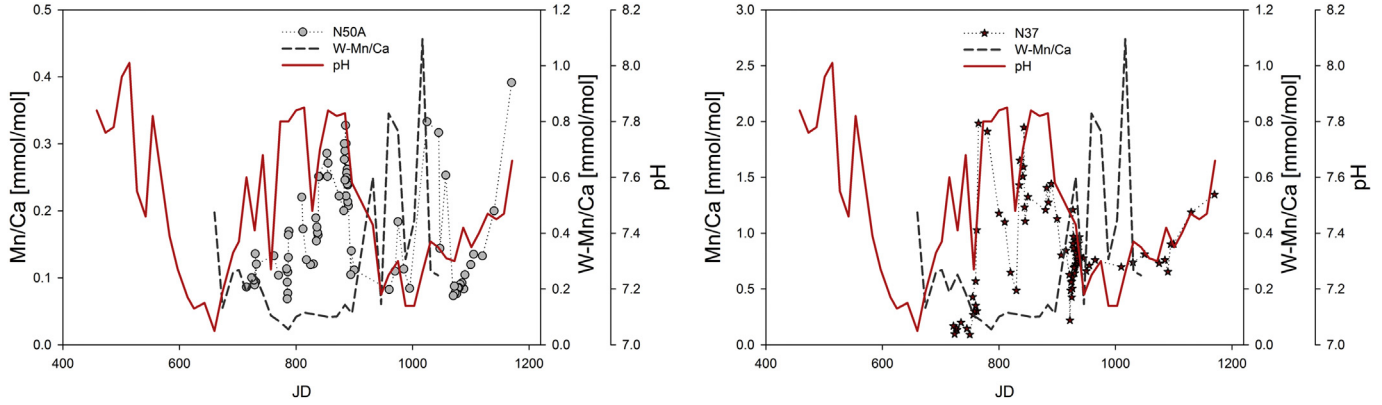

Fig. 6. Mn/Ca ratios of the two *A. dahomeyensis* shells (various symbols) from the Niger River plotted with water pH (solid line). The x-axis represents Julian date (JD), calendar days, starting from Jan 01, 2010, derived from the $\delta^{18}O$-based age models.

whose suggestions and constructive comments helped to further improve this manuscript.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemgeo.2018.04.026.

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